ATC White Paper

TBN Titration Methods (ASTM D2896 vs ASTM D4739)

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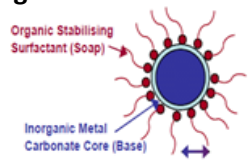
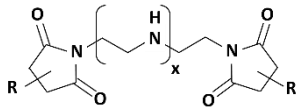
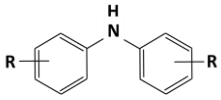
What are ASTM D2896 and ASTM D4739?

ASTM D2896 and ASTM D4739 are both potentiometric titration methods used for determination of basic constituents (alkalinity reserve) in petroleum products. Measurements are made by addition of an acid to the lubricating oil, then monitoring the amount of acid required to neutralize the base content of the lubricant. The measurement of base is reported as total base number (TBN), the equivalent concentration of potassium hydroxide base with units of mgKOH/g.

What's different between the ASTM D2896 and ASTM D4739 methods?

The ASTM D2896 and ASTM D4739 methods can be run using the same titration equipment. However, there are some key differences to the titration solution and solvent system used, which are listed in the table below.

	ASTM D2896	**ASTM D4739**
Titration Solution	Perchloric acid ($HClO_4$) pK_a = -10	Hydrochloric acid (HCl) pK_a = -7
Solvent System	Glacial acetic acid; chlorobenzene	Isopropanol; toluene; chloroform
Features	Highly precise method (R and r are low). Fully titrates strong and weak base.	Less precise method (R and r are high). Fully titrates strong base only.
Additives Titrated		
Detergents 	✓ 100%	✓ 100%
Ashless Dispersants 	✓ 100%	✓ Partially
Amine Antioxidants 	✓ 100%	✗ 0%

ASTM D2896 uses a stronger acid as the titrant (perchloric acid, pK_a = -10) compared to ASTM D4739 (hydrochloric acid, pK_a = -7). This means that during the ASTM D2896 titration strong and weak bases will be titrated, whereas in the ASTM D4739 titration weak bases may be titrated to a lesser degree of titration, or may not be titrated at all.

D4739 titration is performed by adding fixed amounts of HCl at fixed time intervals, whereas D2896 is a dynamic method, adding smaller amounts of acid closer to the inflection point for improved precision.

ASTM D2896 uses glacial acetic acid as part of the solvent system, whereas ASTM D4739 does not. The presence of glacial acetic acid increases the sharpness of the inflection point (via a mechanism

called “levelling”), making the inflection point detection more precise in ASTM D2896 relative to the ASTM D4739 measurement.

Why do we have two methods?

ASTM D4739 was developed to provide a base number titration exclusively for tracking used oil base number loss in service. Test Method ASTM D2896 is primarily used for new oils and is used in setting specifications since it is more precise for fresh oils than Test Method ASTM D4739. However, ASTM D2896 suffers two shortcomings when measuring the TBN of used oils; i) weak bases and contaminants such as soot particles present in the used oil lead to inflection point flattening, and therefore a loss of precision; ii) weakly basic degradation products in the used oil will be titrated, thus giving a false value of essential basicity. For these reasons ASTM D4739 was developed with a weaker acid titrant, such that it measures only stronger bases. The ASTM D4739 test method states that “*when the loss of base number value, as the oils proceed in service, is the consideration, this test method is to be preferred and all values including the unused oil shall be determined by this test method.*”[1] However, in practice there is often not a single clear inflection point for determining used oil TBN by ASTM D4739. The reported TBN value is then determined by quite complicated rules related to an inflection window and when the potential matches that of a standard buffer potential. Used oil TBN by ASTM D4739 should be understood as more of an indicator of the trend for TBN depletion as the oil ages in service and not necessarily as an absolute precise value for the TBN reserve. As the ASTM D4739 test method states *“this test method is not intended to, and does not, result in reported basic properties that can be used under all service conditions to predict performance of an oil.”*[1]

ASTM D4739 was not intended to replace ASTM D2896 as a fresh oil TBN measure, with the ASTM D4739 test method stating that *“Test Method D4739 shall be used exclusively for the purpose of tracking base number loss as an oil proceeds in service.”*[1]

Why ASTM 2896 is the preferred method for measuring fresh oil TBN?

The ASTM D2896 method was primarily established for the purpose of measuring fresh oil TBN. When loss of base number in service is being measured by ASTM D4739, a TBN value of the unused oil is taken by the same method for comparison purposes only. However, the ASTM D4739 method is not sufficiently precise to be regarded as reliable method for setting specification limits for new oils.

ASTM D2896 has a greater stated level of repeatability (r) and reproducibility (R) than ASTM D4739. This is a result of the more precise method of ASTM D2896. The two methods quote repeatability (r) and reproducibility (R) as the following: ASTM D2896 Precision Statement;[2] Repeatability All oils with forward titration: r = 3% of Mean. Reproducibility All oils with forward titration: R = 7% of Mean. ASTM D4739 Precision Statement;[1] Repeatability Fresh oils and additives: $r = 0.11(X + 0.0268)^{0.79}$. Reproducibility Fresh oil and additives: $R = 0.42(X + 0.0268)^{0.79}$
To illustrate the increased precision of ASTM D2896 we consider the example of a fluid with a mean measured value of TBN = 10 mgKOH/g, 8 mgKOH/g, or 6 mgKOH/g:

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[1] ASTM International. *D4739-17 Standard Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration*. West Conshohocken, PA; ASTM International, 2017. doi: https://doi.org/10.1520/D4739-17

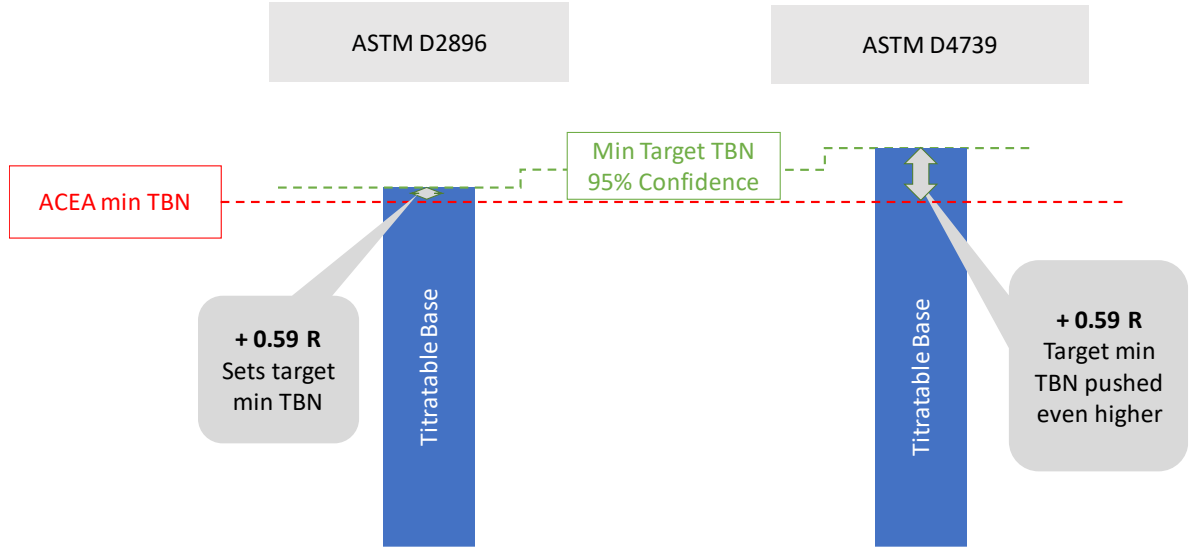
[2] ASTM International. *D2896-15 Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration*. West Conshohocken, PA; ASTM International, 2015. doi: https://doi.org/10.1520/D2896-15

	Mean Measured TBN (mgKOH/g)		
	10.0	8.0	6.0
ASTM D2896			
r	0.30	0.24	0.18
R	0.70	0.56	0.42
ASTM D4739			
r	0.68	0.57	0.45
R	2.60	2.18	1.74

The higher precision of ASTM D2896 is noted in the method for ASTM D4739; "*Test Method D2896 is for new oils and is used in setting specifications since it is more accurate than Test Method D4739… When the base number of the new oil is required as an expression of its manufactured quality, test method D2896 is preferred, since it is known to titrate weak bases that [ASTM D4739] test method may or may not titrate reliably*."[1]

A consequence of the much poorer reproducibility of ASTM D4739 is that for any TBN limit set by this method, the real or target TBN value of the lubricant has to be set significantly higher than the limit to ensure that measured values are above the limit with 95% confidence (95% confidence limits are calculated as: **[limit] ± (0.59 * R) = [limit]**, e.g. 10 + 0.59 * 2.6 = 11.5)[3] as depicted in Figure 1. The problem is further compounded by the fact that for measured TBN levels ≥ 10 by ASTM D4739, the TBN value is only reported to a precision of 1 mgKOH/g. For TBN by ASTM D2896, the TBN values of relevance for fully formulated engine oils are always reported to a precision of 0.1 mgKOH/g.

Figure 1. Depiction of the increase in oil base content that would be driven by the poor precision of a TBN limit set by ASTM D4739.



Can TBN values measured by ASTM D2896 and ASTM D4739 be interconverted?

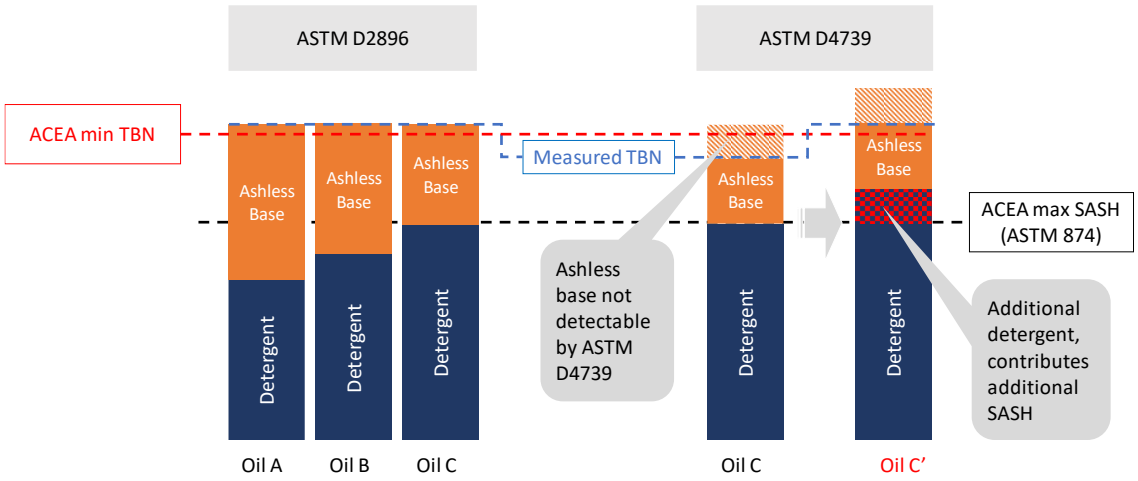
Modern engine oil formulations do contain ashless basic additives such as ashless dispersants and aminic antioxidants. They contribute to fresh oil TBN by ASTM D2896 but are not, or only partially, titrated by the ASTM D4739 method. Because ASTM D2896 titrates a greater range of base strengths,

[3] ISO 4259: Petroleum and related products — Precision of measurement methods and results.

TBN values measured by ASTM D2896 will be higher than those measured by ASTM D4739. This difference is recognised in the ASTM D4739 method which states *"In many cases, the test methods will provide different results."*[1] The relationship between TBN as measured by ASTM D2896 and ASTM D4739 will be highly formulation dependant, and therefore no universal conversion factor will exist between TBN measured by the two methods.

Consequently, setting equal TBN limits for oils measured by both methods is not possible. A varying amount of additional detergent base will be required to bring formulations from a given TBN value as measured by ASTM D2896 to a similar value as measured by ASTM D4739 (see Figure 2 below). Concomitantly, this would also lead to a trade-off between TBN and sulfated ash (SASH) since detergent base is the predominant contributor to sulfated ash. Such a trade-off, as well as the changes to the detergent system, would have significant ramifications to engine oil function across a wide range of performance criteria set by ACEA and OEM specifications.

Figure 2. Depiction of the TBN/sulfated ash trade-off that would be driven by the introduction of fresh oil ASTM D4739 limits.



Summary of ATC Position

- ATC recommends that ACEA removes the ASTM D4739 TBN method from the ACEA 2021 LD specifications.
- ASTM D4739 is not recommended for setting a fresh oil TBN specification.
- ASTM D4739 is not a suitable method for determining a precise value for the TBN of a fresh oil, due to unreliable titration of all base species.
- A performance specification (ACEA 2021 Oil Sequences) is not an instrument to gather data via Rate and Report requirements.
- ASTM D2896 limits cannot be directly converted to ASTM D4739 limits as the two methods are not equivalent and no universal conversion factor exists since differences depend on the additive types and amounts in the oil formulation.
- Transferring the same limit from an ASTM D2896 measurement to an ASTM D4739 measurement implies an increase in the amount of ash containing detergent in the formulation. This would require a TBN / sulfated ash trade-off.